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31 May 1988

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

Attention: Richard O. Ulsh

Reference: Contract DAAL03-87-C-0028

Dear Mr. Ulsh:

Enclosed please find six copies of Spire's Final Report (FR-10109) entitled "Diamond Films by Ion Beam Deposition" for the above referenced contract.

Please contact Dr. Anton Greenwald or Dr. James Hirvonen if you have any questions regarding this report.

Sincerely,

SPIRE CORPORATION

Judy Breen

Judy Breen
Publications Coordinator

JB:ddk

cc: Dr. Carl Nelson, SDIO (1)
Dr. M. Littlejohn, U.S. Army Research Office (1)
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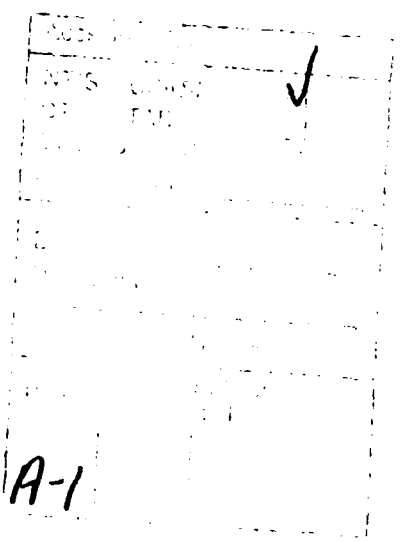


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May 1988

A Final Report for:

# DIAMOND FILMS BY ION BEAM DEPOSITION

Prepared under:

Contract DAAL03-87-C-0028

Submitted to:

U.S. Army Research Office

Research Triangle Park, NC 27709-2211

Prepared by:

Anton C. Greenwald, Ph.D.

James K. Hirvonen, Ph.D.

Submitted by:

SPIRE CORPORATION

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# FOREWORD

Diamond-like films potentially valuable as X-ray lithography masks were fabricated by high rate ion beam deposition using a non-mass analyzed ion source. The high deposition rate reduced the percent of impurities found in the film under normal high vacuum conditions, and left a very hard, continuous and uniform surface. The crystal structure of the film could not be ascertained but it was not epitaxial with the structure of the silicon substrate.

Mass analyzed ion beam deposition was the original experiment intended for this research. Very careful design of a deceleration lens to ensure correct energy of ions decelerated from 35 keV to 100 eV was successfully implemented. However, the current density achieved on the target was under 100 microamperes/$cm^2$. The deposition rate achieved was less than 3 nm/hour. Although the vacuum system was pumped down and baked out and maintained at the lowest possible level consistent with ion implanter operation ($10^{-7}$ torr), residual oxygen gas contamination entering the film exceeded 10 atomic percent, and the films were also not epitaxial with the substrate.

Non-mass analyzed ion beam deposition can be commercialized with reasonable throughput and final coat of the proposed product. This technology could provide superior masks for the next generation of photolithography of submicron features.

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## ABSTRACT

Mass analyzed and non-mass analyzed ion beams were used to deposit carbon films on silicon wafers. Extremely hard, dense coatings that have diamond properties (as opposed to i-carbon) were achieved with high current beams of ionized methane and argon. Residual contaminants of nitrogen and oxygen were minimized. Films deposited by low current mass analyzed beams were heavily contaminated by oxygen. The films are not considered suitable substrate for electronic devices, but are potentially valuable for use as X-ray lithography masks.

## A. STATEMENT OF THE PROBLEM STUDIED

Appropriately doped diamond is a semiconductor material with an extremely high band gap, high carrier velocity, high radiation resistance and high operating temperature capability. Attempts to grow diamond films on silicon so as to integrate the two types of devices have failed.[1]

The objective of this Phase I research was to investigate ion beam deposition (IBD) of carbon as a method to deposit diamond films on silicon in selected areas so that very high speed devices, and/or ultraviolet optical sensors could be integrated with silicon ICs for readout and control.

IBD is a vacuum process. It differs from sputtering in that the energy of the incident ion is reduced to the point where the sputtering yield is less than one; i.e., fewer than one atom is ejected from the substrate for each incident ion. The maximum energy for which this can be observed differs for each ion mass but is typically less than 1 keV for all species. Because the thermal equivalent temperature of the incident ion is so high, the final structure of the deposited film may take forms not available to thermal processes. Hence the growth of diamond films at very low temperatures and pressures may be possible by IBD. Chemical vapor deposition has not been satisfactory.[1]

Diamond has a smaller lattice constant than silicon so that epitaxial growth of a film on silicon directly may not occur. The original proposal called for experiments on grapho-epitaxy,[2] or crystal growth forced by small etched features on the substrate, and experiments on heteroepitaxy on boron-nitride films deposited on silicon. Actual experiments concentrated on deposition on silicon substrates directly, as this proved difficult enough, and tested deposition on salt crystals with the intent of removing the film to study its crystal structure.

Background contamination is another problem seen with experiments on depositing diamond films. Hydrogen must be included in the ion beam to prevent the formation of graphite. Oxygen must be excluded. The use of a high energy ion implanter was proposed as the facility could allow sputter cleaning of the substrate with argon, or another inert gas species, prior to deposition to remove residual surface oxide; and the facility would allow the use of a mass analyzer to insure the purity of the ion beam.

## B. SUMMARY OF THE MOST IMPORTANT RESULTS

IBD of diamond films with a mass analyzed beam failed, while deposition with a non-mass analyzed beam produced a hard transparent film with an index of refraction close to that of diamond.

Film deposition with a mass analyzed decelerated carbon beam had a very low growth rate, under 10 nm/hour. The resulting film contained significant concentrations of oxygen, over 30% atomic, and the experiment was dropped in favor of non-mass analyzed deposition so as to obtain higher deposition rates. Self-sputtering of the film by the ion beam did not reduce the deposition rate.

Film deposition using a non-mass analyzed ion beam had a high growth rate, over 100 Angstroms/minute, and produced a very hard coating (Knoop hardness over 1000) with an index of refraction close to that of diamond (2.4 to 2.5). This film contained less than 5% oxygen, nearly all of which may have been a spurious signal in the analysis technique, and less than 0.2% argon which was used as a diluent gas in the ion beam.

## C. LIST OF ALL TECHNICAL PUBLICATIONS

No technical publications have been produced at this time; however, an abstract will be submitted to the Materials Research Society Symposium A, Processing and Characterization of Materials Using Ion Beams, scheduled for this November, 1988. Papers presented at this meeting will be published in the MRS Symposium proceedings series and acknowledgement will be given to the source of funding..

## D. SCIENTIFIC PERSONNEL

All work on this program was performed by Dr. Anton C. Greenwald and Dr. James K. Hirvonen. There were no graduate students involved and no personnel will apply this research to any part of the work required for an advanced degree.

## E. PHASE I RESULTS

### E.1 Mass Analyzed Deposition

The key facility used for accelerating the ion beam and mass analyzing was a Varian-Extrion 200-1000 with a nominal beam current of 1.0 mA. The beam is extracted from the final magnet without electrostatic scanning into a large chamber where a

rotating fixture normally allows material to be implanted (silicon wafers) by means of being scanned mechanically in front of the fixed beam.

To obtain a low energy ion beam, about 100 eV, it is necessary to run this facility at about 35 keV extraction energy for the ions to have measurable current at the port, and then decelerate the ions to zero potential. The electrostatic lens used for this is shown in Figure 1 and schematically in Figure 2. The lens is constructured so that the electric fields will focus the beam as it decelerates to prevent beam blowup from electrostatic forces. This lens was connected directly to the extraction power supply of the accelerator in series with a bias power supply as shown in Figure 3. This arrangement reduces the variation in ion energy with fluctuations in the accelerating voltage. High frequency ripple could still affect the ion energy as the particles move slowly compared to the speed of light and the time delay as the particles traversed the mass analyzer would allow for some voltage variation. Note that a 0.003% variation between the accelerating and decelerating high voltages would produce a 10% variation in the final ion energy at the substrate surface.

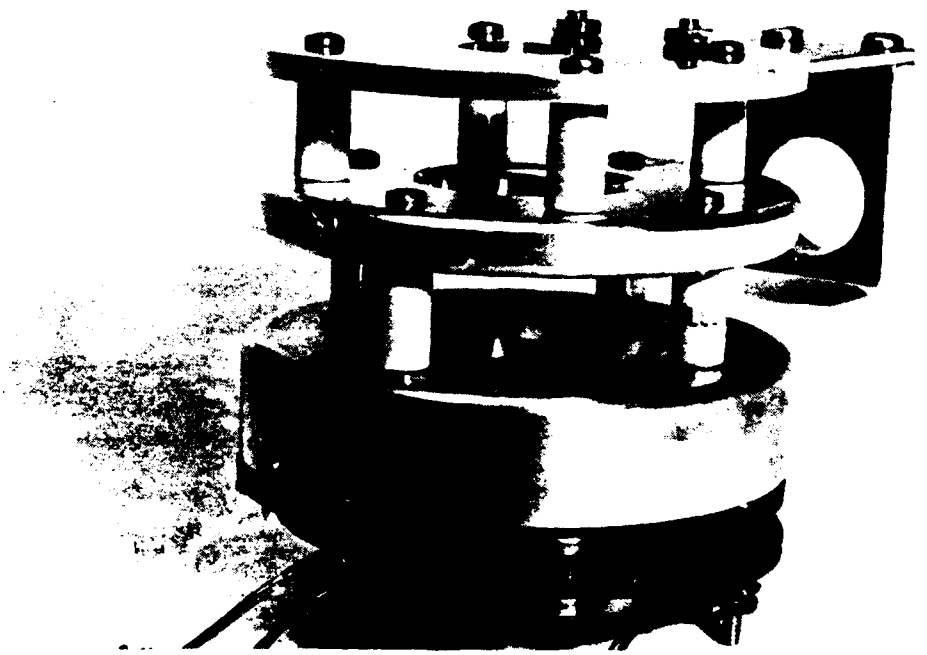


FIGURE 1. PHOTOGRAPH OF THE DECELERATION LENS USED FOR MASS ANALYZED ION BEAM DEPOSITION.

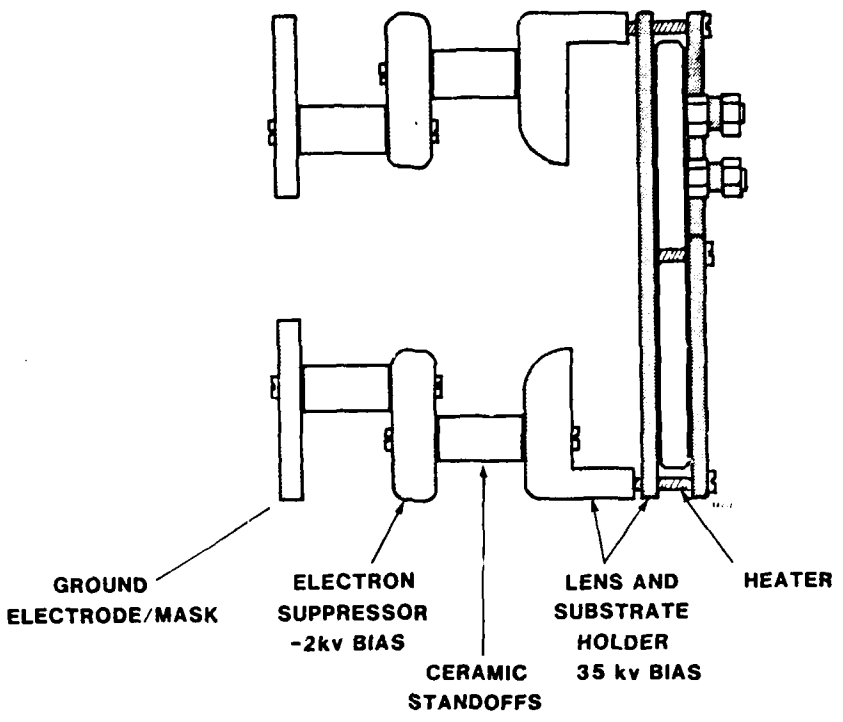



FIGURE 2. SCHEMATIC DIAGRAM OF THE DECELERATION LENS SHOWN IN FIGURE 1.

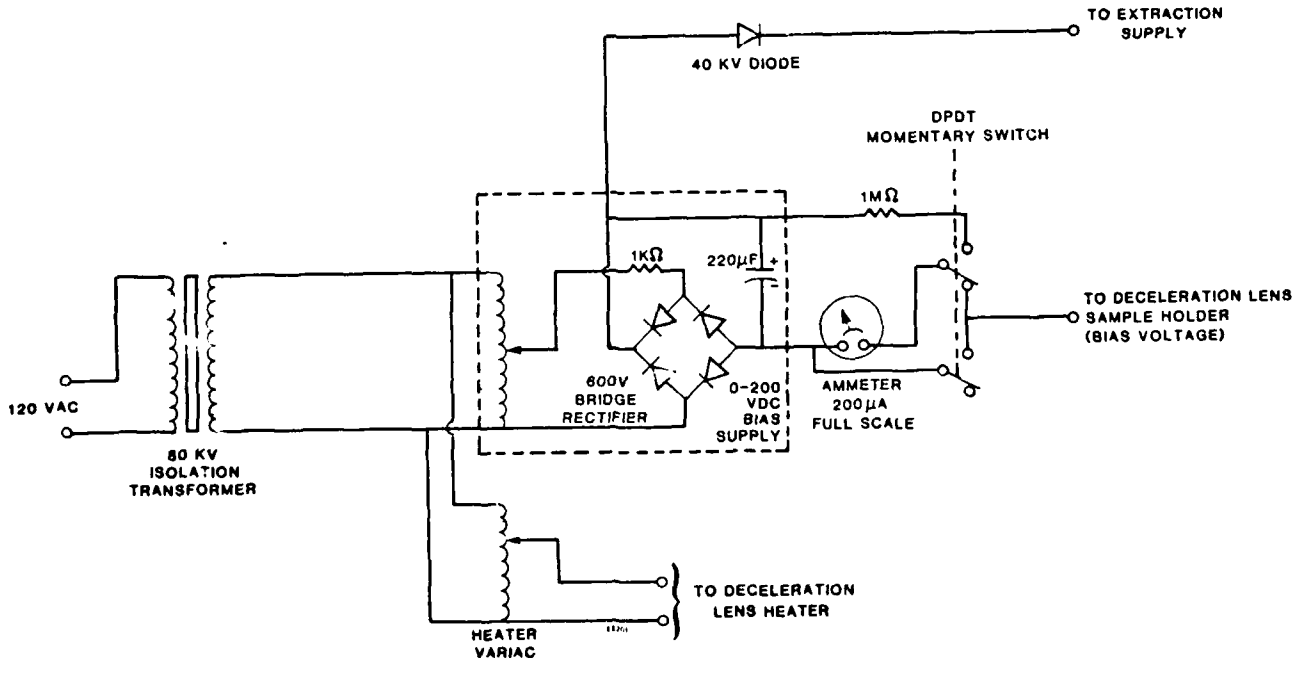



FIGURE 3. ELECTRICAL DIAGRAM OF THE INSTALLATION OF THE DECELERATION LENS SHOWING THE ISOLATED BIAS POWER SUPPLY AND ISOLATED HEATER POWER SUPPLY.

Severe arcing problems with the physical geometry of the setup prevented deposition experiments with this deceleration lens until near the end of the program. Experiments were transferred to the non-mass analyzed equipment described in the next section. Only one deposition run for $10^4$ seconds was made with the deceleration lens.

The results of this run are shown in Figure 4, an ESCA profile of the composition of the film. The silicon seen at the surface is due to atomic mixing between the film and the substrate. The concentration of silicon would be expected to be significantly reduced in thicker films. The high oxygen content could be a surface contaminant so the film was sputter etched for one minute which would normally be sufficient to remove about 20 to 30 Angstroms of silicon dioxide. The atomic concentrations of elements in the film (excluding hydrogen) are shown in Table 1 below. The film was very thin, and it contained a very high oxygen content. The low deposition rate is believed responsible for the high level of contamination seen as even a low partial pressure of oxygen would deposit a thin film on the surface of a sample in three hours, and given an ion beam to drive it in, this would account for the oxygen in the film. Figure 5 shows an electron channeling pattern of the substrate to the side of the deposited carbon layer, showing its crystal structure clearly, and the pattern (or lack of one) seen from the area covered by the carbon layer. The film did not grow epitaxially, certainly the high oxygen content would have prevented it.

TABLE 1. ATOMIC COMPOSITION OF FILMS.

| | Mass Analyzed | Non-mass Analyzed |
|---|---|---|
| Ar | 0.0 | 0.2 |
| C | 24.0 | 91.5 |
| Cu | 0.0 | 0.5 |
| N | 0.0 | 3.1 |
| O | 34.4 | 4.5 |
| Si | 41.4 | 0.0 |

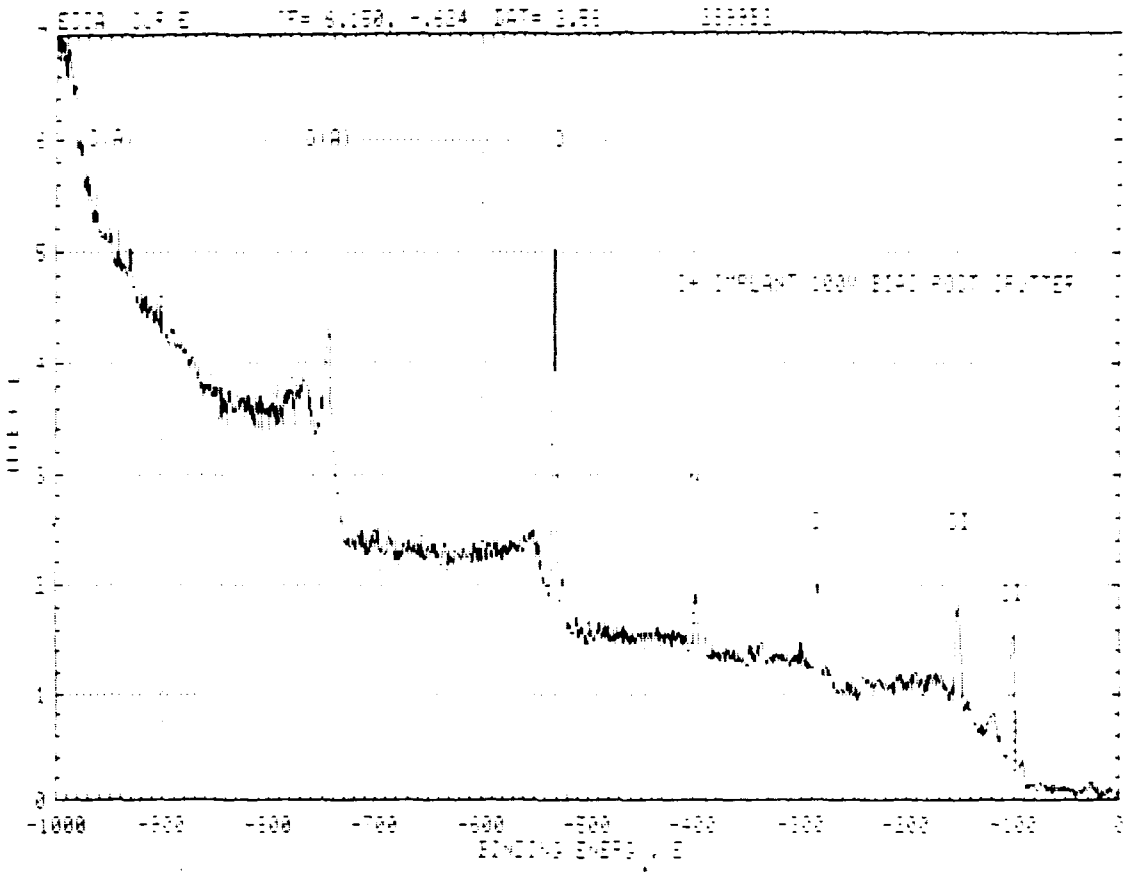
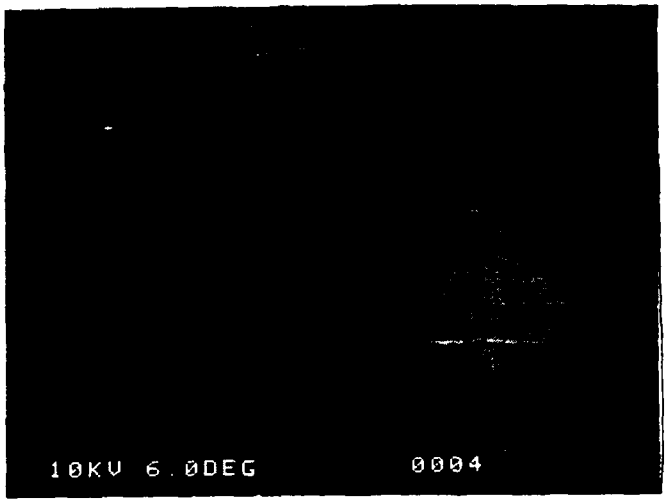
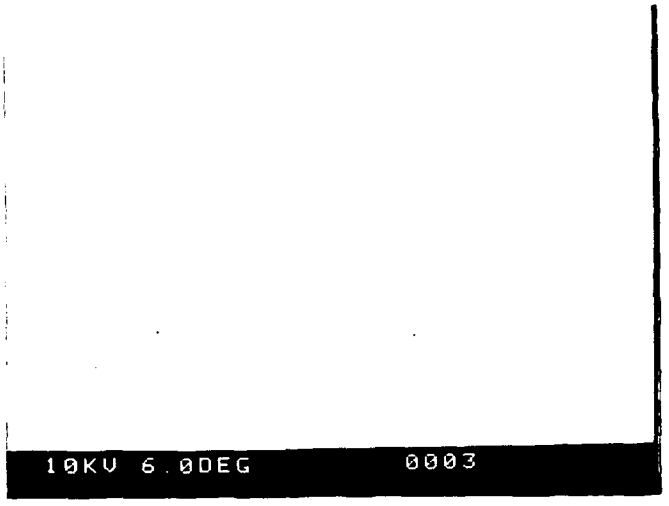


FIGURE 4. ESCA SURVEY OF MASS-ANALYZED IBD FILM AFTER SPUTTERING FOR ONE MINUTE.




**(A)**




**(B)**

FIGURE 5. ELECTRON CHANNELING PATTERNS SEEN IN IBD FILMS ON SILICON.

(a) Substrate

(b) Film

## E.2 Non-Mass Analyzed Ion Beam Deposition

The different techniques tested to deposit a diamond film are listed in Table 2. They include the direct ion beam deposition (IBD) of methane ($CH_4^+$) as well as the IBD of a combined argon plus methane beam ($Ar^+$ plus $CH_4^+$) and finally Ion Beam Enhanced (Assisted) Deposition (IBED) of evaporated carbon films. The purpose of the argon was twofold; to help sustain the ion source as well as providing more nuclear energy loss in the deposition to promote more thermal spikes or displacement collisions thought responsible for creating the local "high-temperature," high pressure regions necessary to form diamond-like films.

The system used to produce these consisted of a high-current, low energy Kaufman type ion source coupler to an electron beam evaporation unit, shown schematically in Figure 6 and pictorially in Figure 7. The ion source was operated in the energy range where previous researchers have seen DLC formation and high enough to not be beam current limited by space charge considerations. The initial depositions used a 3:1 ratio of $CH_4$ to Ar pressure into the ion source. This produced too high a sputtering yield with no net deposition occurring. This prompted using less argon (i.e., 10:1 $CH_4$ to Ar pressure ratios) for subsequent runs. Operating with pure methane produced other problems including deterioration of the filament (i.e., formation of tungsten carbide) or the buildup of an insulating layer on the source chamber which quenches the plasma before significant deposition can be performed. The evaporation of carbon was carried out using a electron beam evaporator utilizing a graphite block as a charge source and a quartz crystal oscillator to monitor the deposition rate.

For all cases the measured hardness of the thin DLCs was higher than that of the Si substrates (KHN = 900 at 5 gms). Only one deposition ($Ar^+$ onto evaporated carbon) did not involve hydrogen as a constituent of the ion beam and the coating produced in this manner displayed extremely fast deterioration when exposed to atmosphere as a result of stress and/or chemical reactivity indicating the importance of incorporating hydrogen in these films for stability.

The variations of the thickness and microhardness are due in part to the falloff of evaporant on the substrate positioned at 45° to both the evaporant flux and ion beam as shown in Figure 6. In addition there are local variations ($\pm$ 15%) within the beam profile affecting sputtering rates and stoichiometries.

## TABLE 2. ICN BEAM DEPOSITION AND ION BEAM ASSISTED DEPOSITIONS USED TO PRODUCE DIAMOND-LIKE COATINGS ON Si

| DLC Description | Deposition Parameters | Thickness (Angstroms) | Knoop Hardness KHN (5 gm) | Refractive Index (n) Thickness | Friction -( ) Steel $Si_3N_4$ | Comments |
|---|---|---|---|---|---|---|
| $CH_4^+$ plus $Ar^+$ 3:1 | (111) Si substrate R.T. deposition 400 eV, 500 A/cm$^2$ beam | - | 1150 | No results absorbing film | 0.24-0.74<br>0.2<br>10:1 | More sputtering than deposition, go to leaner mixture |
| $CH_4^+$ | (111) Si, R.T. 1 hr run 400 eV, 130 A/cm$^2$ | - | 1200 | 1.52-1.65 | 0.2<br>0.18 | |
| $Ar^+$ beam onto evaporated carbon | (111) Si, R.T. 400 eV, 100 A/cm$^2$, 1-8 Å/sec | - | 1000 | 2.45-2.51 | 0.23<br>0.21 | Deposit on glass witness plate exfoliated immediately upon exposure to air |
| $CH_4^+$ plus $Ar^+$ (10:1) beam onto evaporated C | (111) Si, R.T. 400 eV, 300 micro A/cm$^2$ 3-5 Å/sec (30 min) | 2000-2900 | 1400-1700 | 2.1-2.2 | - | |
| $CH_4^+$ plus $Ar^+$ (10:1) on evap. C | (111) Si, 400° substrate, 400 eV, 300 A beam 3-6 Å/sec (25 min) | 5200-7200 | 1300-1900 | 2.55-2.63 | - | |
| $CH_4^+$ plus $Ar^+$ (10:1) on evap. C | (111) Si, R.T. 400 eV, 120 A/cm$^2$ 0.5-1.5 Å/sec (20 min) | 1600-2750 | 1200-1400 | 2.50-2.65 | - | Selected area seeded with diamond polishing compound with no effect noted. |
| $CH_4^+$ plus $Ar^+$ (10:1) | (100) Si, 400°C 500 eV, 350 A (50 min) | 1400 | 1600 | 2.30-2.45 | 0.3<br>0.19 | |
| Ar sputtering C onto Si while simultaneously bombarding deposited carbon | (111) Si, R.T. 1000 eV $Ar^+$ sputter beam (1.2-1.7 A/cm$^2$) 150-300 μA | 2100-2800 | 1130-1250 | 2.50 | 0.8<br>0.7 | R.T. = room temperature about 25°C |

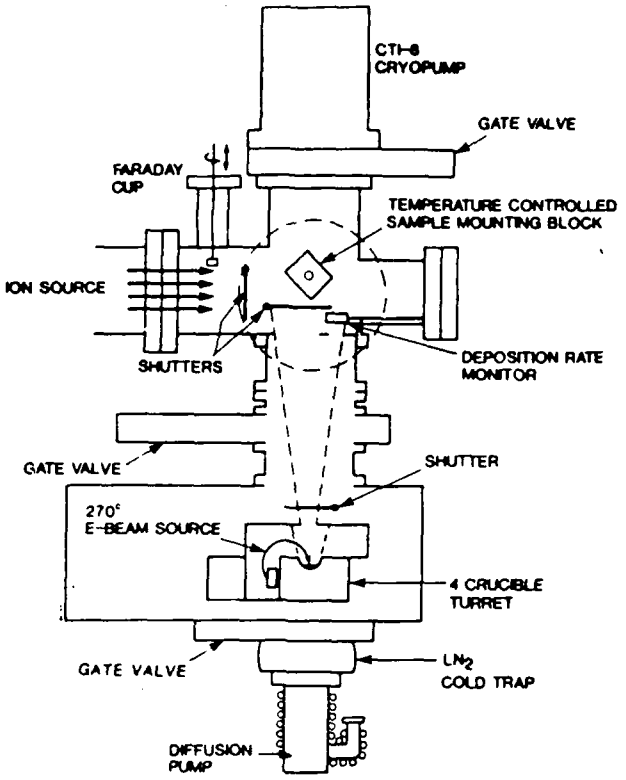



FIGURE 6. SCHEMATIC OF SPIRE'S IBED SYSTEM.

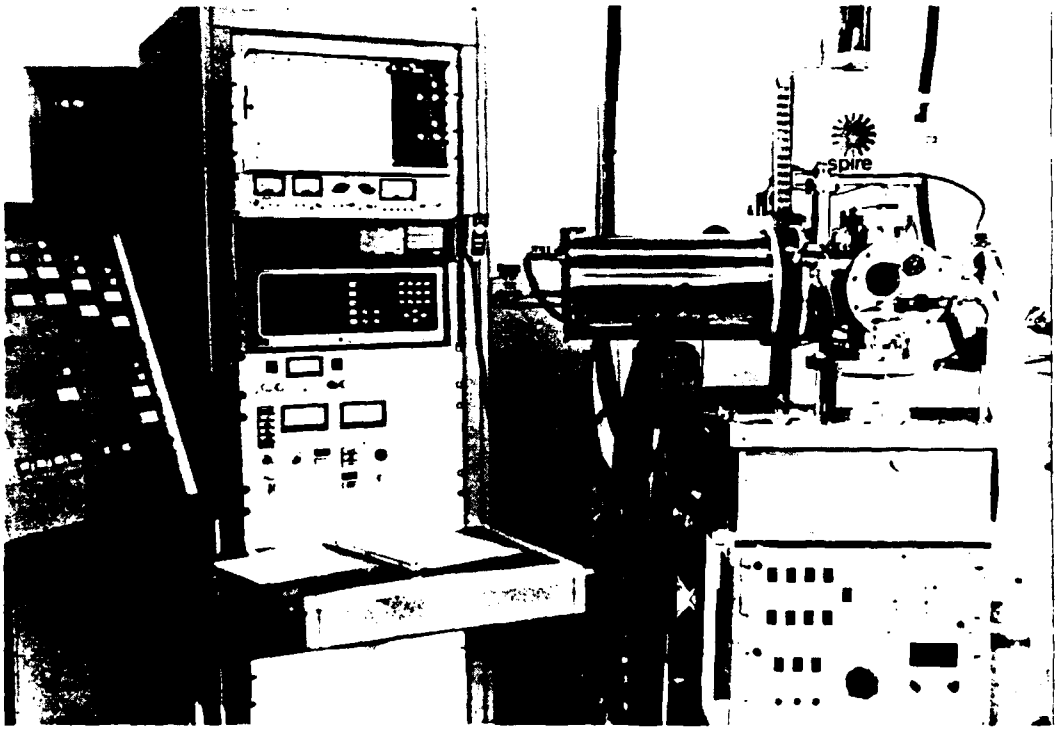



FIGURE 7. PHOTOGRAPH OF IBED SYSTEM.

An ESCA survey for the film deposited by using a 10:1 methane/argon ratio with no evaporation is shown in Figure 8. Comparing the results to Figure 4, contamination has been significantly reduced.

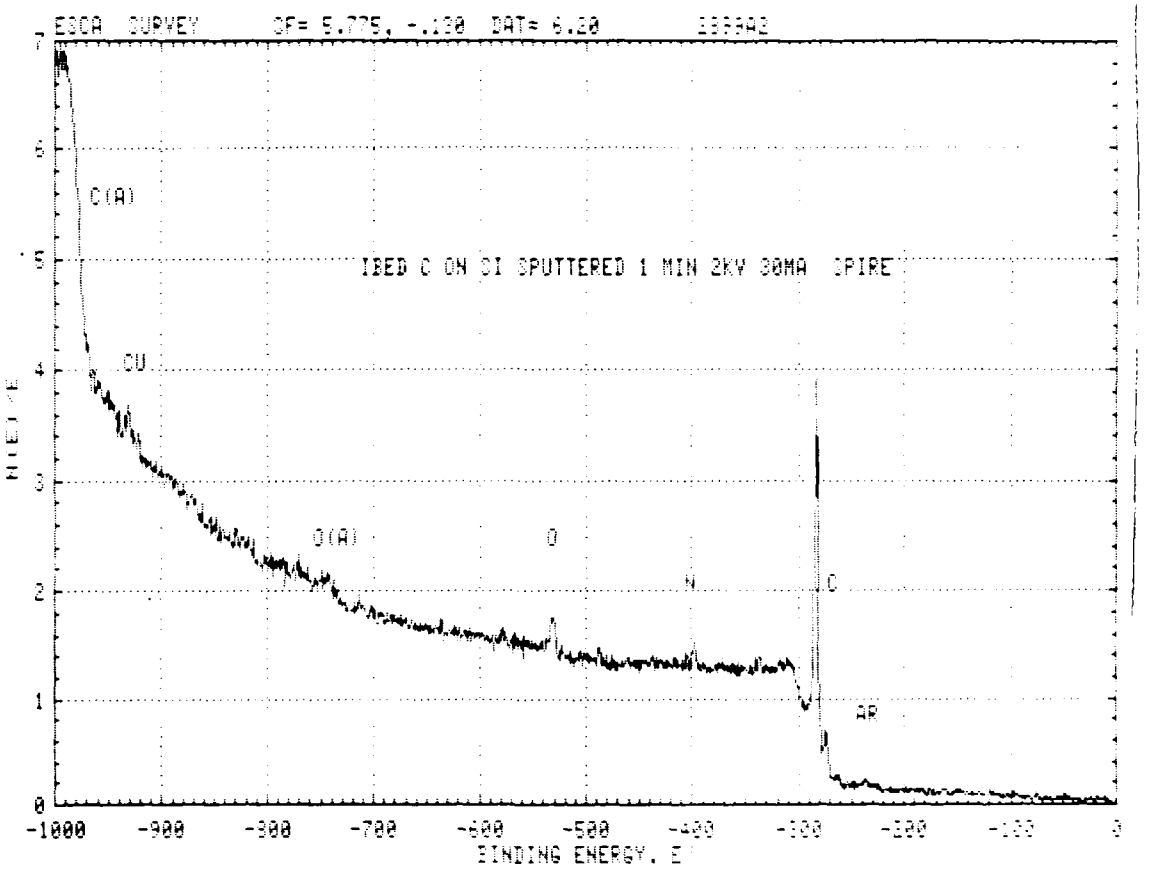



FIGURE 8. ESCA SURVEY OF NON-MASS ANALYZED IBD DIAMOND FILM AFTER ONE MINUTE SPUTTERING.

F. REFERENCES


1. S. Matsomoto and Y. Matsui, J. Mat. Sci., 18, 1785 (1983).

2. H. Sith et al., J. of Crystal Growth 63, 527 (1983).